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TORONTO UNIV (ONTARIO) DEPT OF CHEMISTRY
STUDY IN MOLECULAR LASERS.(U)

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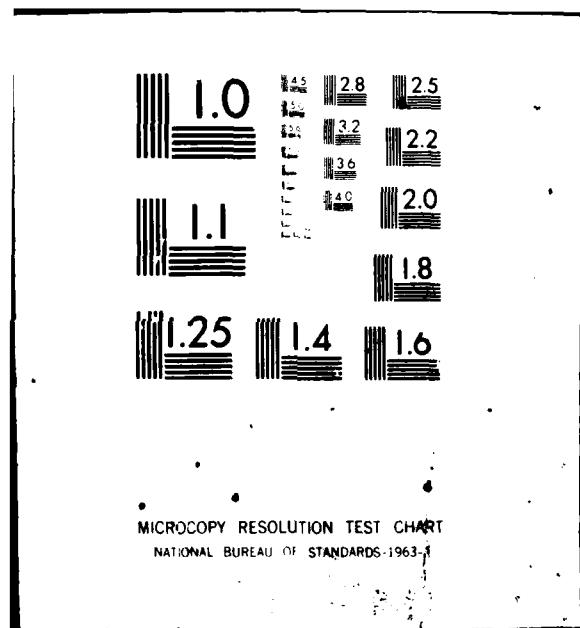
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In addition to Final Technical Report, the present research resulted in thirteen other publications. These can be divided into four separate groups, which are discussed below.

I: Atomic Recombination Reactions by Flash Photolysis Over a Wide Temperature Range

a) Critical evaluation of existing atomic recombination^{2,9,11}

Since no review on the subject had been written for a considerable time, the principal investigator evaluated the available experimental data, in order to (1) determine which data are more urgently needed, (2) determine which results are obsolete and can be ignored, (3) reveal experimental aspects important to the theory of recombination-dissociation reactions, and (4) pin-point systematic and random errors, which limit the accuracy of rate measurements. His experimental work in project I is, and will continue to be, influenced by these evaluation. Specially, with respect to halogen reaction a separate manuscript was written⁹:

Halogen recombination-dissociation reactions.

Current status. R.K. Boyd and G. Burns, J. Phys. Chem. 83, 88-98 (1979).

Recombination and dissociation rate constants for halogens, obtained by a variety of experimental techniques, are assembled and compared. In general, more accurate and precise rate constants are obtained by more recent investigators, who learned from the experience of

their predecessors. Surprisingly, a large amount of data on recombination of halogen atoms, in the presence of even the simplest third bodies, is still not available. On the other hand, much of the available data can now be considered quite reliable. Trajectory calculations yield the recombination rate constants in fair agreement with experiments.

Data on heteropolar recombination of I and Cl, obtained by a group at University of Pennsylvania, were reanalysed¹⁰ and made consistent¹⁰ with the remainder data available on I, Br and Cl recombination. In addition, the following study^{3,7} was performed:

Recombination of iodine atoms by flash photolysis over a wide temperature range. VII. Recombination between 206 and 300°K. H.W. Chang and George Burns, J. Chem. Phys. 64, 349-353 (1976).

Recombination of iodine atoms was studied by flash photolysis of HI at 205 and 300°K. The photolysis produced both H and I atoms. However, under present experimental conditions, the reaction $H + HI \rightarrow H_2 + I$ was completed within the duration of the flash, thus eliminating reactive hydrogen atoms and yielding additional quantities of iodine atoms. Condensation of solid I_2 on cold walls of the reaction vessel was found to be much slower than iodine recombination reaction. For these reasons I atom recombination could be studied without interference of side reactions. At 206 K the recombination rate constants in He, Ar and Xe were found to be

(in $10^{-9} \text{ l}^2 \text{mole}^{-2} \text{sec}^{-1}$) 2.8, 7.9 and 15.8 respectively, which agree well with the rate constants obtained earlier between 300 and 1200°K [J.K.K. Ip and G. Burns, J. Chem. Phys. 56, 3155 (1972)]. Recombination rate constants in H_2 and D_2 , 7.8×10^9 and $7.7 \times 10^9 \text{ l}^2 \text{mole}^{-2} \text{sec}^{-1}$, respectively, agree reasonably well with earlier experimental results obtained at elevated temperatures [H.W. Chang and G. Burns, J. Chem. Phys. 59, 1043 (1973)]. It was found that the recombination rate constants of iodine atoms in HI can be expressed by the following equation, valid between 206 and 300°K: $\log k_r^{\text{HI}} = 10.47 - 3.5 \log(T/300)$. This last reaction appears to occur via the radical-molecule complex mechanism. The intermediate radical in this reaction may be a relatively stable hydrogen bi-iodide, in which case the activation energy of the reaction $\text{IHI} + \text{I} \rightarrow \text{IH} + \text{I}_2$ should not be negligible. Alternatively, the intermediate could be an unstable I-IH radical, in which iodine atom may interact with both atoms of HI. However, in this case weak chemical forces involving interaction between two halogen atoms would predominate. At 487 nm iodine absorption coefficients ratio $\epsilon(206^\circ\text{K})/\epsilon(300^\circ\text{K})$ is equal to 1.15.

Recombination of iodine atoms by flash photolysis over a wide temperature range. VIII. I_2 . R.E. Antrim, George Burns and J.K.K. Ip, Can. J. Chem. 55, 749-756 (1977).

Flash photolysis of I_2 in a large excess of O_2 was studied between 300 and 1173 K. Between 573 and 1173 K the rate of atomic recombination $2\text{I}({}^2\text{P}_{3/2}) + \text{O}_2({}^3\Sigma_g^-) =$

$I_2(^1\Sigma_g^+)$ + $O_2(^3\Sigma_g^-)$ was measured without interference of side reactions. Its rate constant was found to be $\log K_r^0 2(T) = 9.000 - 9.71 \log(T/573)$. Between 573 and 873 K there is an induction period lasting several hundred microseconds during which only a small net change in the iodine molecule concentration takes place. This induction period is consistent with the reaction $O_2(^1\Delta_g) + I_2 = O_2(^3\Sigma_g^-) + 2I$. Below 573 K, the overall recombination rate constant has a temperature dependent negative temperature coefficient and is enhanced when the flash includes radiation in the neighborhood of 200 nm. Evidently this occurs because the flash photolysis of O_2 creates new efficient third bodies, such as O_3 and $O_2(^1\Delta_g)$, which accelerate the recombination reaction either directly or via an IO intermediate. The mechanism for the formation of IO during the flash photolysis of I_2 in an excess of O_2 was studied. It was shown that the reactions $O(^3P) + O_3^* + I_2 = IO + I + (O_2)$, where O_3^* refers to an electronically or vibrationally excited state of O_3 , account for the formation of IO under our experimental conditions. IO may possibly be formed via the reaction $O_3^* + I = IO + O_2$. On the other hand, reactions between excited or ground state I atoms and O_2 suggested by earlier workers do not occur. Thus, all experimental complications observed are traceable to the presence of O_2 photolysis products and to the reaction of $I(^2P_{1/2})$ with $O_2(^3\Sigma_g^-)$.

II. Diatom Dissociation Reaction in Shock Waves^{1,8}.

Dissociation of Br₂ in shock waves. R.G. Macdonald, George Burns and R.K. Boyd, J. Chem. Phys. 66, 3598-3608 (1977).

The rate of dissociation of Br₂ in the presence of Ar and Br₂ has been investigated using three independent experimental techniques in the same shock tube: molecular absorption spectroscopy (AS), two-body emission spectroscopy (ES), and laser schlieren technique (LS). Present results yield recombination rate constants in good agreement with each other and with earlier high temperature flash photolysis data. The temperature range over which dissociation was studied was extended from 1200 to 3000°K. Recombination rate constants can be summarized in terms of the following equations: $\log_{10} k_r^{\text{Ar}}(\text{LS}) = 8.251(\pm 0.002) - 1.36(\pm 0.29) \log_{10}(T/2300)$ or $\log_{10} k_r^{\text{Ar}}(\text{LS}) = 8.378(\pm 0.001) - 1.05(\pm 0.30) \log_{10}(T/2300)$. The difference between these two equations arose because in the first equation $R_{\text{Br}} = R_{\text{Br}_2}$ was assumed, while in the second $R_{\text{Br}} = R_{\text{Kr}}$ was used. Here R_x is the Gladstone-Dale constant of X. These equations are valid between 1600 and 3000°K. The analogous equations for $k_r^{\text{Br}_2}$ are: $\log_{10} k_r^{\text{Br}_2} = 8.718(\pm 0.001) - 2.35(\pm 0.41) \log_{10}(T/1900)$ and $\log_{10} k_r^{\text{Br}_2} = 8.767(\pm 0.001) - 2.18(\pm 0.42) \log_{10}(T/1900)$, valid between 1500 and 2000°K. The laser schlieren technique, as applied to chemical reactions in shock waves, was studied. In particular, the effect of finite width laser beam, optical absorption of reacting gas, temperature dependence of its refractive

and hence polarizabilities, of reaction products. Although generally these properties are not known, they can be estimated empirically.⁸

In addition a similar study on Br₂ dissociation in Kr was performed¹.

III. Trajectory Studies of Recombination-Dissociation Reactions^{4,6,12,13}.

Trajectory study of atomic recombination reactions. VII. Recombination of I and Br Atoms, D.T. Chang and George Burns, Can. J. Chem. 54, 1535-1542 (1976).

Classical 3-D trajectory investigation of bromine and iodine atom recombination reactions in He, Ar and Xe, performed earlier, are extended, using an improved sampling technique, to include a larger number of trajectories and a wider temperature range (200-1500 K). The three body potential energy surfaces used were assumed to be nearly additive, but otherwise were defined by the existing molecular beam and spectroscopic data and contained essentially no arbitrary parameters. The agreement between computed and experimental rate constants is reasonable, and is best if the third body is heavy and reaction proceeds via a bound complex as IXe. Orbiting inert gas-recombining atom intermediate dimers, XM*, where X = I or Br, contribute to the overall recombination reaction via XM* + X → X₂ + M reaction, provided M is heavy. If M = He, this reaction path is negligible at all temperatures studied, again provided that X = I or Br.⁴

Trajectory study of dissociation reactions. Br_2
in Ar at 3500 K. D.T. Chang and George Burns, Can. J.
Chem. 55, 380-382 (1977).

Dissociation of Br_2 in Ar was studied at 3500 K using classical 3-D trajectory technique, and compared with earlier trajectory calculations. Some of the assumptions used previously were eliminated, while others were studied in some detail. The one-way flux, equilibrium rate coefficient, obtain from over 8400 trajectories, was found to be over an order of magnitude larger than the experimental rate constant. This was taken as an indication that at high temperatures the nonequilibrium effects are important in dissociation reactions. In order to understand these effects better, additional calculations using an improved set of assumptions were performed. The calculated dissociation rate constant for $\text{Br}_2 + \text{Ar} \rightarrow 2\text{Br} + \text{Ar}$ which accounted for nonequilibrium effects, agrees reasonably well with the experimental results.⁶

Trajectory study of dissociation reactions. The single-ensemble method. H.D. Kutz and G. Burns, J. Chem. Phys. March 15 issue (in press) (1980).

A new method for the calculation of nonequilibrium effects in diatom dissociation reactions is presented. It is based on the use of a single statistical ensemble, which is studied by the multiple collision 3-D trajectory calculation technique. Statistical fluctuations, which in the past prevented accurate determination of such observables as steady state rate constants and reaction

cross sections, have now been reduced by a factor of better than ten, as compared with earlier work. Such an improvement in statistical error makes possible the detailed study of various features of the nonequilibrium steady state. Several approximations of earlier multiple-collision trajectory calculations are examined, and results on the dissociation of Br_2 in Ar at 3500°K are presented. For this particular system in the steady state, the internal energy bias parameter was found to be equal to three.¹²

Trajectory study of atomic recombination reactions.

The energy transfer mechanism. G. Burns and A.W. Young, J. Chem. Phys. March 15 Issue (in press) (1980).

Earlier classical 3-D trajectory investigations of the energy transfer mechanism for halogen atoms recombining in the presence of an inert gas assumed an arbitrary initial separation between the diatom quasidimer X_2^* and the inert gas atom. As a result the calculated rate constants varied with the initial conditions chosen. In the present work, calculations were performed with the initial I_2^* -He separation properly averaged, and with various maximum internuclear separations, r_{\max} , for the I_2^* dimer. The overall agreement between calculated and experimental results is reasonable.¹³

IV. Study of Br_2 Continuum⁵.

Diatom potential curves and transition moment functions from continuum absorption coefficients. Br_2 .

R.J. McRoy, R.G. Macdonald and George Burns, J. Chem. Phys. 65, 1485-1500 (1976).

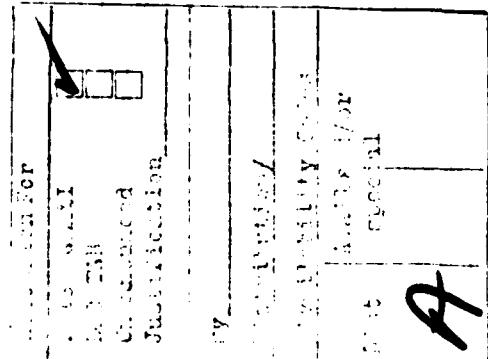
A program for calculating diatomic molecule absorption coefficients using "exact" numerically computed radial wavefunctions was developed and used to examine critically a number of approximations which are frequently used in absorption coefficient calculations. These tests showed that both use of the delta function approximation, and fixing the rotational quantum number in the radial overlap integrals at $J = 0$, introduce errors of $\approx 4\%-6\%$ of the absorption coefficient maximum ϵ^{\max} . Similarly, errors of $\approx 1\%-2\%$ of ϵ^{\max} are introduced by either fixing the initial state J at the average value for the given temperature, or by using Gislason's Airy-function approximation for the unbound state wavefunction. A simple procedure for shrinking the sum over initial state J 's without significant loss of accuracy was therefore devised. These techniques were then applied to the analysis of the visible absorption continuum of Br_2 , and a nonlinear least-square fitting procedure used to determine optimized final state potential curves and transition moment functions for the two overlapping electronic transitions. In the region to which the data are sensitive, $2.10 \leq R \leq 2.55 \text{ \AA}$, the transition moments so obtained (in debyes, lengths in angstroms) are $M_0(R) = 0.3905 + 0.265(R - 2.3)$ for the $\text{B}({}^3\Pi^+_0_{0u}) \leftarrow \text{X}({}^1\Sigma^+_g)$ transitions and $M_1(R) = 0.5060 - 0.154(R - 2.3)$ for the $\text{B}({}^1\Pi^+_{1u}) \leftarrow \text{X}({}^1\Sigma^+_g)$ spectrum. The concomitant repulsive potential curves for the $\text{B}({}^3\Pi^+_0_{0u})$ and $\text{B}({}^1\Pi^+_{1u})$ states are, respectively (in cm^{-1} , expressed relative to the ground state dissociation limit; lengths in angstroms):

$V_0(R) = -1175 + 5494 \exp[-5.807(R - 2.3)]$ and $V_1(R) = 7654 \exp[-4.637(R - 2.3) - 0.879(R - 2.3)^2]$, where the former expression applies only to the region inside the B-state inner turning point for $v = 8$, $R_1(8) = 2.4485 \text{ \AA}$. Comparisons with experimental relative intensities in the discrete portion of the B-X spectrum, and with molecular beam photofragment spectroscopy measurements of the relative strengths of the two electronic transitions, are also reported.

Publications

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3. "Recombination of Iodine Atoms by Flash Photolysis over a Wide Temperature Range. VII. Recombination between 206 and 300°K", H.W. Chang and George Burns, J. Chem. Phys. 64, 349-353 (1976).
4. "Trajectory Study of Atomic Recombination Reactions. VII. Recombination of I and Br Atoms", D.T. Chang and George Burns, Can. J. Chem. 54, 1535-1542 (1976).
5. "Diatom Potential Curves and Transition Moment Functions from Continuum Absorption Coefficients" Br_2 ", R.J. LeRoy, R.G. Macdonald and George Burns, J. Chem. Phys. 65, 1485-1500 (1976).
6. "Trajectory Study of Dissociation Reactions. Br_2 in Ar at 3500 K", D.T. Chang and George Burns, Can. J. Chem. 55, 380-382 (1977).
7. "Recombination of Iodine Atoms by Flash Photolysis over a Wide Temperature Range. VIII. I_2 ", R.E. Antrim, George Burns and J.K.K. Ip, Can. J. Chem. 55, 749-756 (1977).

8. "Dissociation of Br_2 in Shock Waves", R.G. Macdonald, George Burns and R.K. Boyd, J. Chem. Phys. 66, 3598-3608 (1977).
9. "Halogen Recombination-Dissociation Reactions. Current Status", R.K. Boyd and G. Burns, J. Phys. Chem. 83, 88-98 (1979).
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